DATA EVALUATION RECORD

STUDY 9

CHEM 036101 Trifluralin §163-3

FORMULATION--90--EMULSIFIABLE CONCENTRATE (EC)

STUDY ID 40673601D
Soderquist, C.J., D.G. Crosby, K.W. Moilanen, J.N. Seiber, J.E. Woodrow. 1975. Occurrence of trifluralin and its photoproducts in air. J. Agric. Food Chem. 23:304-309.

DIRECT REVIEW TIME = 10

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CONCLUSIONS:

Mobility - Field Volatility

This field volatility study provides supplemental data. It cannot be used to fulfill the data requirement (163-2). These data were taken from published articles and were not originally designed to satisfy Subdivision N data requirements. Therefore, it is difficult to draw the conclusions needed for an environmental fate assessment. However, these data and the other published volatility data submitted (MRID 40673601A, 40673601B, 40673601C, 40673601E, 40673601F, 40673601G) do indicate the following:

1. Volatility may be a major route of dissipation for trifluralin.
2. Trifluralin appears to volatilize (≈25 to 60% of applied in 11 days).

3. Laboratory volatility data are needed to determine relative rate of dissipation due to volatility in relation to other routes of dissipation.
4. No further field volatility data are needed until evaluation of acceptable laboratory volatility data is completed.

In this study the concentration of trifluralin in the soil immediately posttreatment was not reported. Therefore, the application rate was not confirmed and the concentration of trifluralin in the air could not be related to the amount of trifluralin in the soil. Furthermore, the study was terminated before the pattern of decline of the test substance was established.

METHODOLOGY:

Field volatility

Trifluralin (Treflan EC, concentration not specified, Elanco Products) was surface applied at 1.7 kg/ha to a bareground plot (15 m X 15 m) in California (soil not characterized) in June 1973. Lovol samplers (0.03 m^3/min) were installed at 0.5 and 1.8 m above the soil surface; a Hivol sampler (1 m^3/min) was installed at 0.5 m above the soil surface. A portable weather station was located adjacent to the plot; 2.8 days after pesticide application, the plot was irrigated (3 cm). Air samples were collected immediately after, and for 7 days posttreatment. For 7 days, the Lovol samplers were run for 10 hours/day and the Hivol sampler was run for 3 hours/day at midday. The morning after each sampling interval, the absorbent was removed from the sampler, placed in foil-covered flasks, and returned to the laboratory. In the laboratory, 100 mL of acetone was added to the flasks, and the mixture was stored at -10 C until processing (length of time not specified). The acetone was shaken with the absorbent for 1 hour and the acetone was decanted and filtered; the absorbent was extracted again with acetone. The filtrates were combined, brought to volume, and an aliquot was concentrated and analyzed by GLC with electron capture detection.

Trifluralin (Treflan EC, concentration not specified, Elanco Products) was surface applied at 0.9 kg/ha to a bareground, disked field (61 ha) in California (soil not characterized), in April 1974. The trifluralin was then incorporated to a depth of 15 cm by disking, and the field was planted to safflower. For 12 days, the Hivol samplers were run for 4 hours/day. Air and soil samples were collected as previously described.

Twenty soil samples were collected each day from random sites in the plot. Cores were composited and frozen in foil-lined bags until processing (length of time not specified). Soil samples were extracted with benzene:2-propanol (50:25) by shaking for 30 minutes. The soil slurry was allowed to settle and the liquid was partitioned with aqueous sodium chloride solution to remove the 2-propanol. The ben-

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zene was dried over sodium sulfate and analyzed by GLC as previously described. If the soil was wet, acetone was used for soil extraction instead of benzene. The method detection limits were 0.01 ppm.

DATA SUMMARY:

Trifluralin (Treflan EC), surface applied to a bareground plot at 1.7 kg/ha, was volatile with a maximum concentration of 2570 ng/m^3 trifluralin in the air 0.5 m above the soil surface on day 3 posttreatment (Table III). Average soil concentrations of trifluralin decreased from 2.03 ppm at 1 day posttreatment, to 0.45 ppm at 7 days posttreatment (Table IV).

Trifluralin (Treflan EC), applied at 0.9 kg/ha and incorporated to a soil depth of 15 cm, was volatile with a maximum concentration of 155 ng/m^3 in the air 0.5 m above the soil surface on day 5 posttreatment, when a rainfall event occurred (Table V). The amount of trifluralin in soil samples ranged from 0.42 to 0.88 ppm during the twelve days of sampling (Table V).

COMMENTS:

1. The concentration of trifluralin in the soil immediately posttreatment was not reported although samples were collected at this time. Soil data were reported for 1 day posttreatment; the percent volatiles, also reported for this sampling interval, indicated that significant volatilization had already occurred. Therefore, the application rate was not confirmed and the concentration of trifluralin in the air could not be related to the concentration of trifluralin in the soil.

2. The study was terminated before the pattern of decline of trifluralin was established. For the non-incorporated plot, the soil concentration of trifluralin apparently decreased over 7 days, but insufficient data were presented to evaluate the decrease; for the incorporated plot, the amount of trifluralin in the soil varied without a discernible pattern during the 12 days of the study.

3. The test soils were not characterized.

4. Field conditions and weather data were not reported.

5. Volatility was not expressed as g/ha/day.

6. The vapor pressure of trifluralin was not reported.

7. The trapping efficiency of absorbent in the samplers was not reported.

8. The study authors also examined photoproducts found in the air above the non-incorporated plot; two degradates, compounds II and III, were

present at 12.4 ng/m^3 and 0.73 ng/m^3 at day 3 posttreatment (Table III). These compounds were not further identified. The study authors reported that TLC silica gel plates, developed by hexane, were used to separate photoproducts from trifluralin. Areas were scraped, eluted with acetone, and analyzed by GLC.

9. The initial portion of the paper, which addressed the photodegradation of volatile products in the laboratory, was not included in this review since these data are not pertinent to the Field Volatility Data Requirement.

10. The study authors suggested that since trifluralin was incorporated to a 15-cm depth, the increase of trifluralin content in the 7.5-cm layer from 0.48 ppm at 1 day posttreatment to a maximum of 0.88 ppm at 7 days posttreatment indicates that trifluralin moved up in the soil profile due to transport by evaporating water.

11. This study is one of several published papers included as appendices to MRID 40673601 (Day, E.W. 1988. Laboratory and field volatility studies with trifluralin from soil. Laboratory Project ID. EWD8807). This document was submitted as an assessment of the potential inhalation hazard of trifluralin to exposed workers. Because this portion of the document contains summary data only and is not pertinent to Subdivision N guidelines, it was not reviewed; only the published papers in the appendices have been reviewed.

12. EFGWB prefers that [^{14}C]residues in samples be separated by chromatographic methods (such as TLC, HPLC, and GC) solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the R_f of reference standards.

    In this study aliquots of the extracts were analyzed by GLC.

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STUDY AUTHOR(S)'S RESULTS AND/OR CONCLUSIONS

(INCLUDING PERTINENT TABLES AND FIGURES)

RESULTS AND DISCUSSION

Laboratory Photolysis. The photoreactor was designed so that a light beam shining through the substrate vapor would not intercept the walls, except at the end of the flask where a small window allowed light to exit into a light trap. Alternatively, wall irradiation, and hence surface-induced photoreactions, could be promoted by replacing the light trap with a spherical reflector (Crosby and Moilanen, 1974). Irradiation of trifluralin in the reactor under normal conditions (i.e., with the light trap) resulted in conversion to a number of products, and reflection of light onto the reactor wall produced no discernible change in the amount or nature of photoproducts. Trifluralin vapor was stable in the dark.

The dinitrotoluidines II and III, benzimidazoles IV and V, and benzimidazole precursors VI, VII, VIII, and IX, reported by Leitis and Crosby (1974) were detected (Figure 2). Short term irradiation produced primarily II while longer irradiation (12 days) resulted mainly in IV and V

Table I. Vapor-Phase Photoproducts of Trifluralin

Compound	R_f value[a]	Amount, mg[b]
I	0.60	0.7
II	0.52	0.3
III	0.40	0.1
IV	0.39	2.1
V	0.23	1.7

[a] Amount found after irradiation of 5 mg of I for 12 days. [b] Silica gel G (0.5 mm) developed in hexane–acetone (3:1).

(Table I). Irradiation of IV resulted in its facile conversion to V which was resistant to further photolysis. All of the volatile photoproducts were identified by comparing their R_f values, retention times, and mass spectra with those of authentic standards. In addition to the volatile products, a highly colored (orange-brown) band remained at the origin of the tlc plate. Characterization of this band following elution with warm methanol employed a thermal degradation method (Leitis and Crosby, 1974) in which the eluted material was subjected to glc analysis. The resulting pattern of three peaks indicated the presence of the benzimidazole precursors reported by Leitis and Crosby (1974) (Figure 2): 2,3-dihydroxy-2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazoline (VI); 2,3-dihydroxy-2-ethyl-7-nitro-5-trifluoromethylbenzimidazoline (VII); 2-ethyl-7-nitro-5-trifluoromethylbenzimidazole 3-oxide (VIII), and 2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazole 3-oxide (IX).

The vapor-phase photolysis of trifluralin involves both oxidative dealkylation and cyclization. Photochemical N-dealkylation of amines appears to be a free-radical oxidation by atmospheric oxygen (Sharkey and Moebel, 1959). Benzimidazole formation, reported by Crosby and Moilanen (1972) and Crosby and Leitis (1973), has been confirmed for similar dinitroaniline herbicides (Newsom and Woods, 1973; Plimmer and Klingebiel, 1974; Niles and Zabik, 1974). These cyclization reactions may be accounted for (Leitis and Crosby, 1974) by a modification of the free-radical mechanism proposed by Dopp (1971) to explain the photochemical formation of indole *N*-oxides

Table II. Trapping Efficiencies for Trifluralin and Its Photoproducts from Air[a]

Compd	Recovery,[b] %	
	1.0 μg[c]	25 μg[c]
I	40 ± 7	48 ± 4
II	36 ± 4	61 ± 10
III	49 ± 8	67 ± 11
IV	85 ± 10	91 ± 10
V	84 ± 5	101 ± 5

[a] Air at 30° (125 ml[a]) processed with Hivol Sampler. [b] Average and standard deviations of three determinations. [c] Amount introduced onto the filter.

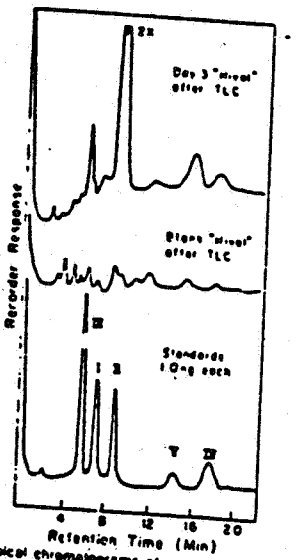

Figure 3. Typical chromatograms of a sample, blank, and standard compounds I–V.

from nitroaralkanes. The proposed mechanism is consistent with vapor-phase conditions, since it represents light-induced polarization of the nitro group and subsequent intramolecular rearrangements which do not require external reagent. Photolysis in I in the absence of oxygen produced exclusively IV.

Photolysis of trifluralin films, solutions, and coated soils was also carried out. For example, the irradiation of suspended dust coated with I gave results essentially identical (half-life of 2.5 hr at 20 ppm on standard test dust) with those obtained by irradiation of I on soil in a Petri dish (half-life of 2.2 hr at 50 ppm on Dinuba fine sandy loam soil). In general, it appears that I decomposes faster in solution, as a thin film on glass, and when adsorbed to soil or suspended dust than as a vapor, although difficulties inherent in measuring the rate of vapor-phase photolysis have precluded confirmation of this view.

Trifluralin and photoproducts II–IV are all photolabile; V, however, appears to resist further photolysis. For example, irradiation of V at 20 ppm on suspended standard test dust for 3 hr resulted in its quantitative recovery. Prolonged irradiation (200 hr) of V in the vapor-phase

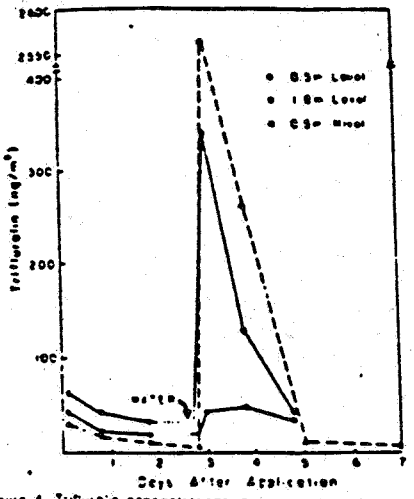

Figure 4. Trifluralin concentrations in air over a surface treatment plot

photoreactor confirmed that V should be considered a persistent, relatively stable product.

Air Sampling Techniques. Air sampling techniques for pesticides usually consist of drawing air through a solvent-filled bubbler or impinger (Miles *et al.*, 1970). Drawbacks to this method include a restricted sampling rate (<0.2 m³/min) which necessitates long sampling periods, and expensive and fragile glassware often inconvenient for portable use. Solid trapping agents offer an alternative to liquid absorption methods (Seiber and Woodrow, 1974). The system adopted for the trifluralin studies utilized a filter bed consisting of Chromosorb A coated to 5% with paraffin oil although several other solid trapping agents were effective. Trapping efficiencies for vapors of trifluralin and its photoproducts (determined by spiking the Hivol filter with known amounts of I-V and measuring the per cent of the vaporized material trapped on the solid after 2 hr of sampling) were adequate and reproducible (Table II). Furthermore, extraction recoveries of I-V (2 μg) from the adsorbent exceeded 85%. For analysis of photoproducts II-V, the large excess of I was conveniently removed from air sample extracts by preparative tlc. The chromatograms of Figure 2 illustrate typical results. From the glc response of standards relative to air blanks, the usual detection limits of I-V were calculated to be 0.5–1.0 ng/m³.

Surface Treatment Plot. Following the completion of the laboratory phase of this and method development, several experiments were carried out to check for the presence of I and its breakdown products in the field. In one experiment, I was applied to the surface of bare soil with no incorporation. Although this condition does not reflect application practice recommended by the manufacturer, it afforded enhanced volatilization for the quantitation of I-V in the air. Volatilization was further enhanced by overhead irrigation 2.8 days after application. Samplers placed in the center of the plot indicated concentrations of I of less than 61 ng/m³ for the initial 2.8 days before the dramatic effect of soil moisture on the volatilization rate of I occurred (Figure 4). The concentration of I measured by the Hivol Sampler on day 3 exceeded that of the Lovol Samplers (Figure 4) since the Lovol values are an average of 10 hr of sampling the latter portion of which probably contained much less trifluralin than immediately after water application. The Hivol sample on the other hand is an average of only the first 2 hr after water application when trifluralin volatilization was at its maximum. Trifluralin was still vaporizing after 7 days but at a lower rate than for the 0–2.8 day period.

Analysis of the day 3 Hivol sample for photoproducts (Table III) showed the unmistakable presence of II and III, while the benzimidazoles IV and V were tentatively identified at levels near their detection limit. These results conform to the laboratory model in which II was the initial product, while prolonged irradiation (12 days) yielded primarily IV and V. Since the atmospheric residence time of I before reaching the sampler undoubtedly was quite brief, little localized formation of V was expected or found. The possibility that II-V originated from impurities in the herbicide formulation was precluded by careful analysis of a sample taken directly from the spray tank. Possible degradation of I to II-V on the adsorbent surface was ruled out by their absence from a sample of Chromosorb A spiked with I and used to sample clean air for 2 hr.

Analysis of soil samples showed that residues of I declined from 2.03 to 0.45 ppm in 7 days (Table IV). Photoproducts appeared in the first sample (0.1 day), increased slightly at day 2.7, and declined by day 7. The existence of "polar products" (Probst *et al.*, 1967) and the tentative identification of polar amine derivatives (Leitis, 1973) argue for the existence of other breakdown pathways in addition to photolysis; microbial action probably played a minor role, since I was not incorporated and the soil was extremely dry except during and just after irrigation. Probst *et al.* (1967) concluded that while microorganisms may contribute to the eventual destruction of trifluralin, this cannot be considered a major pathway of degradation.

Soil Incorporation Plot. While the surface treatment experiment was successful in proving the existence of I and some of its photoproducts in air, a similar evaluation under more realistic conditions was clearly desirable. Thus in a second field experiment, I was soil incorporated into a larger area (61 ha).

This time, concentrations of I in the air measured by Hivol Sampler (Figure 5) declined from 12 ng/m³ to less than 1 ng/m³ within 3 days. A heavy rain (0.37 in.) on

Table III. Photoproducts in Air (Surface Treatment, Hivol, Day 3)

Compd	Amt, ng/m³
I	2570
II	12.4
III	0.73
IV	≤0.50
V	≤0.50

Table IV. Soil Residues from Surface Treatment

Days after application	Soil residue, ppm[a]				
	I	II	III	IV	V
1	2.03	0.060	0.005	0.048	0.027
2.7	1.18	0.095	0.014	0.027	0.050
7	0.45	0.057	0.010	0.020	0.028

[a] Averages of three determinations with relative deviations of 16%.

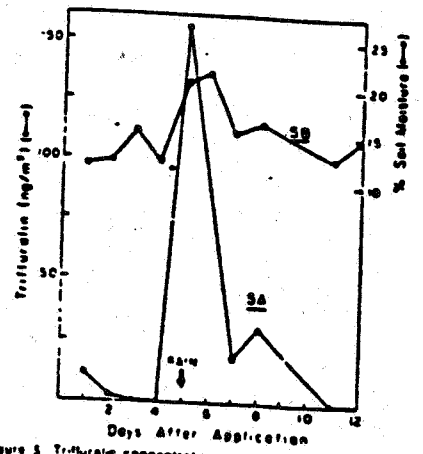

Figure 5. Trifluralin concentrations in air (A) and per cent soil moisture (B) for a soil-incorporated field

day 5 and again between days 7 and 8, increased air levels as in the previous experiment. While the overall appearance of Figure 5A matches Figure 4, the maximum values are significantly less in the former indicating the less drastic effect of water on soil incorporated I. Comparison of concentrations of I to the soil moisture plot (Figure 5B) reemphasizes the correlation between the volatilization rate of I and soil moisture content. A summary of the results of the second experiment is presented in Table V; the presence of II in the air was confirmed by gc-ms analysis of pooled samples 5, 6, and 8, the mass spectrum and retention time being identical with those of II. The fact that I was incorporated to a depth of 15 cm while the soil was sampled to a depth of only 7.5 cm, coupled with the movement of I to the soil surface by moisture, accounts for the trend of increasing concentrations of I in soil with time (Table V).

Source of Photoproducts. While some trifluralin photoproducts (e.g., II) unquestionably were present in the air after both surface treatment and soil incorporation of I, their origin is not as clear. Three potential routes of photoproduct formation must be considered: (1) the photolysis of I vapors in the atmosphere, (2) the photolysis of I on the soil surface followed by volatilization, and (3) the photolysis of I on air-suspended dust. The importance of these routes depends not only on the relative photolysis rates at the appropriate sites, but on transport to the sites as well. For example, the volatilization rate of I from soil into the atmosphere may limit the importance of route 1 more than the rate of vapor-phase photolysis. Since route 3 would significantly contribute to the disappearance of I only in cases of very dry soil and appreciable wind action, will be focused on the other possibilities with specific reference to the formation of II.

Evidence to support the formation of II on soil surfaces (route 2) derives from the laboratory photolysis of I on soil (and on suspended dust) and detection of II in the soil immediately after both surface and soil incorporated application of I in the field. If this route were to predominate, the ratios of II to I in air and soil would be identical after correction for their relative volatilities. If route 1 were significant, the ratio of II to I in the air should exceed that in soil, however, the ratios of II to I in soil and air (soil incorporation experiment, Table V) were essentially identical. The soil ratio ideally should be determined on a sample taken from the top few millimeters of soil where II would be formed, however, the fact that soil was sampled to a depth of 7.5 cm further decreases the significance of route 1 in these experiments.

Nevertheless, vapor-phase photolysis remains undemonstrable. To confirm the laboratory results, I (5 g) was vaporized directly into a field atmosphere from an electrically heated glass tube (5 cm o.d. × 20 cm) by means of a blower within 25 m of a Hivol Sampler placed 1 m above ground. The sampler was run for 15 min while I was being vaporized; analysis indicated 0.55% breakdown of I to II (0.52 μg of II and 94 μg of I trapped) while the unvaporized solid remaining in the tube contained undetectable (less than 0.1%) II as an impurity.

The above field-test data indicate that route 2—photolysis of I at the soil surface followed by volatilization—must predominate. However, while the direct-vaporization experiment shows vapor-phase photolysis to occur at an appreciable rate, the air samples were collected so close to the ground that I vapor would have had only brief residence in the atmosphere. As a major proportion of the trifluralin lost from the soil may move as vapor (Parochetti and Hein, 1973; Savage and Barrentine, 1969), the atmosphere must provide a significant repository in which trifluralin eventually is degraded until only photochemically stable products remain.

Table V. Summary of the Soil Incorporation Experiment

Days after application	Weather conditions: wind[a] & air temp, °C	Air samples[b]				Soil samples		
		I, ng/m³	II, ng/m³	II/I, %	I on filter, μg	I,[c] ppm	II,[c] ppm	II/I, %
1	Light; 23	31.7	0.42	3.0	0.45	0.48	0.017	3.5
2	Heavy; 25	8.7			1.10	0.42	0.014	
3	None; 27	<1			0.23	0.32	0.024	
4	Heavy; 24	<1			0.22	0.65	0.021	
5	Heavy (rain)	155	4.9	3.1	0.28	0.65	0.030	4.6
6	Heavy; 15	91.4	2.4	2.6	0.18	0.52	0.027	5.2
7	Light; 20	17.4	0.44	2.5	0.32	0.58	0.021	3.6
8	Light; 15	31.3	1.0	3.2	0.43	0.71	0.017	2.4
11	Heavy; 31	<1			0.35	0.70	0.02₀	
12	Mist; rain; 28	<1				0.45	0.02₀	
				Av 3.0%				Av 3.6%

[a] Light = 0-5 mph; moderate = 5-10 mph; heavy = >10 mph. [b] Single determinations. [c] Averages of three determinations with relative standard deviations of 17%.